

Photoelectron spectroscopy on a liquid water jet: an exploratory experiment

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INTRODUCTION

Surfaces of volatile liquid solutions can be studied in a high vacuum environment, only, when the surface area is sufficiently small in relation to the molecular mean free path in the vapor phase near the liquid surface. For neat liquid water at room temperature the vapor pressure corresponds to a mean free path in the order of ten micrometer. Exploiting this, we could recently demonstrate the feasibility of photo-electron spectroscopy experiments on a fast flowing jet of liquid water with only 6.3 micrometer diameter [1]. A high flow speed of approximately 120 m s^{-1} prevents excessive cooling of the liquid filament by the free molecular evaporation. It also prevents efficiently the buildup of photoelectric charges on the non-conducting liquid samples. Near the nozzle exit such jets have an unperturbed cylindrical section of two to three millimeter length which is used for the surface photoelectron studies. For the first experiments the 21.2 eV radiation of a HeI light source was employed and photoelectron spectra were recorded using a 10cm radius hemispherical electron energy analyzer. These initial studies show a gas-to-liquid energy shift of the electron binding energies by one to several Electron Volts reflecting the ion solvation enthalpy in chemical solutions. In ongoing PhD work these experiments could be extended to salt solutions and show the solvation energies of halogen anions in water and in further simple dielectric solvents. In a next step it appears desirable to study cations as well in order to clarify the role the orientation of the water solvent molecules in the hydration process. However, the above experiments with He I radiation are restricted to negative electrolyte ions with particularly low ionization energies. The He I studies suffer also from low photoelectron intensities due to the small liquid jet surface. For overcoming these major present restrictions the new third generation synchrotron source with tunable light and with intensities exceeding the focussed He lamp limit of $10^{12} \text{ photons mm}^{-2}$ appears to be ideally suited for proceeding with experiments on liquid water solutions.

WATER JET PHOTOELECTRON TEST MEASUREMENTS AT AN ALS BEAMLIN

For a first functional test of the liquid water jet operation at a synchrotron beam end station the beam line 9.02 appeared most suitable. [2] It is designed as a molecular beam machine and can handle the large amounts of gas evaporating from the volatile liquid jet. In addition, this vacuum apparatus contains a threshold photoelectron spectrometer and employs tunable VUV and XUV radiation, including the familiar He I energy region of our previous studies at liquid jets. For the test a $10 \mu\text{m}$ liquid jet nozzle assembly [1] was installed near the detection center of the threshold photoelectron spectrometer [2]. The available pumping capacity of turbomolecular pumps and of two cryotraps in the liquid jet beam dump had to be extended by a third refrigerator cryopump in the photoionization region in order to reduce the pressure in the experimental chamber to safe limits for the XUV photon beamline vacuum. Eventually, in the

last phase of the test the gas load originating from the 6 μm water jet at 2 centigrade nozzle temperature was still very high at the XUV exit mirror chamber and was only removed temporarily by external liquid nitrogen cooling of the walls of this chamber. The liquid water jet did then run for several hours exposed to the synchrotron photon beam. A Threshold PhotoElectron spectrum for water was measured repeatedly during the last day of this one-week feasibility test. Due to high signal levels, data acquisition was rapid. The spectrum shown in Figure 1 between 11.5 and 21 eV with a step-size of 10 meV was recorded with only 1 second/point acquisition time.

PRESENT RESULTS AND CONCLUSIONS

Unfortunately, the evaluation of two spectra at slightly different photon beam positions showed later that we could not obtain significant difference spectra of the liquid surface and of the water vapor phase contributions in the measured overall spectrum in Fig.1. A further flaw in our here conducted experiment is a poor knowledge of the actual extent of spontaneously occurring electrokinetic charging on our pure water jet. Intentionally, we had not added here a small fraction of salt (10^{-3}m) which usually stabilizes the electrical potential of the liquid jet. This was omitted here in order to avoid salt contaminations in this beamline which are difficult to clean up afterwards. For an accurate energy calibration and for an estimate for the contribution of the

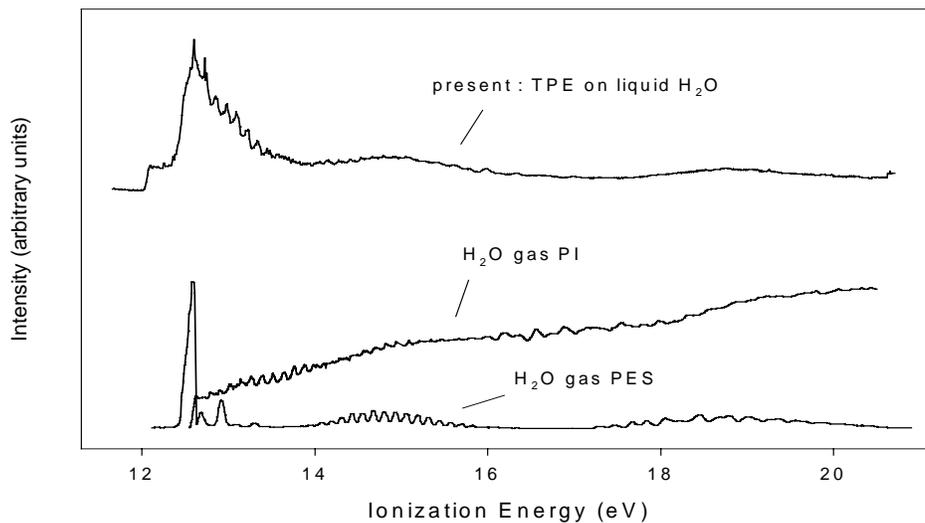


Figure 1. Threshold Photoelectron Spectrum (TPE) obtained on a thin fast flowing jet of liquid water with 6.3 μm diameter. The TPE signal for electrons within 7meV bandwidth is recorded as a function of the undulator radiation for photon energies from 11 eV to 21 eV. The comparison with available literature gas phase measurements of the photoionization spectrum (PI) for H₂O [3] and of a photoelectron energy spectrum (PES) obtained at the He I photon energy of 21.2 eV,[4] allow an assignment of the main spectrum structure to the vapor phase surrounding the liquid jet. In addition, the shoulder in the here measured TPE spectrum, visible at 12 eV to 12.6 eV, can be attributed to the liquid water photoelectron spectrum which is characterized by a 1.2 to 1.4 eV lower ionization threshold. [1]

water vapor phase we use, therefore, the literature photoionization spectrum of water (PI) [3] and a He I photoelectron spectrum (PES) [4], shown in the lower part of Fig. 1. Noteworthy, we could not find a wide range TPE spectrum for gaseous water, although elaborate high resolution TPE and PFI spectra for individual ion vibration states are available in narrow ranges near the ionization threshold (cf [5]).

The three principal peak structures of the PES spectrum at electron binding energies of 12.6 eV, at 14.7 eV and at 18.5 eV, similarly, appear in the photoion spectrum as steps in the ion intensity signal. By comparison of these gas peak signatures with the clearly visible peak structures in the present TPE spectrum we can deduce a (flow induced, electrokinetic) liquid jet charging to approximately 1 volt in the present experiment. The additional shoulder in the TPE spectrum of the liquid water jet, appearing in the range between 12 eV and 12.6 eV, thus, is to be interpreted as a photoelectron signal originating from the liquid water surface. In further detail, however, the different electric field distortions for the gas phase spectrum versus the photoelectron spectrum of the liquid jet surface here prevent a more substantial quantitative interpretation of the liquid spectrum contribution in this preliminary experiment.

In the basic technical and experimental goals of this first brief test for synchrotron radiation photoelectron spectroscopy at a volatile liquid water surface we feel we were fully successful: critical vacuum interface regions between the free liquid surface of the water jet and the ultrahigh vacuum regions of the synchrotron radiation light source have been located and can be optimized in subsequent experiments; in addition, this experiment confirmed that the intensity of 10^{11} photons s^{-1} of high resolution monochromator selected X-UV radiation with 0.1 mm focus spot size allows rapid photoelectron spectrum measurements on volatile micron size liquid jets. The poor liquid-to-gas signal ratio will be improved in future experiments by an appropriate matching of the viewing area of the photoelectron entrance slits to the narrow liquid jet surface width.

ACKNOWLEDGMENTS

Support by the German Science Foundation (DFG) under Foerderungs No. FA 251/5-1 and by the ALS is gratefully acknowledged.

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